Interfacial Characterisation of Sol-Gel Derived Coatings of Hydroxyapatite and Zirconia Thin Films with Anodised Titanium Substrates

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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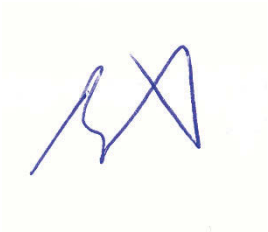

ABSTRACT

The anodisation of titanium involves the formation of a thin, compact oxide layer, which improves the wettability of the oxide film. This process involves the conversion of the rutile structure of the original titanium oxide into a mixed rutile and crystalline anatase structure. An understanding of the anodised structure and how it influences the bonding properties of the sol-gel coating of hydroxyapatite (HAp) and zirconia is the main focus of this research project.

The titanium samples were anodised in a mixed phosphoric acid (H_3PO_4) sulphuric acid (H_2SO_4) solution. The samples were also anodised at three different voltages, 25V, 50V and 75 Volts for 30 minutes. Both anodised and original titanium samples were spin coated with alkoxide-derived hydroxyapatite and zirconia sol-gel coatings and examined using X-ray diffraction and scanning electron microscopy. By controlling the oxide layer formed on the titanium substrates, its thickness and the amount of anatase formed in the mixed oxide layer as well as the oxide films porosity enabled the preparation of an oxide film surface that yielded the optimum conditions for coating with the sol gel solutions.

The diffusion theory can be seen to operating in the coating of the sol gel films through interdiffusion of the sol gel coating into the titanium oxide layer, with zirconium ions detected in the titanium oxide layer up to a depth of 75 microns and in the case of the hydroxyapatite sol gel coating phosphorus and calcium was detected in the titanium oxide layer.

The adhesion of the sol gel coated samples was tested using a micro-adhesion tester and the zirconia samples were further tested on an Ortho-pod tribological tester to determine the wear properties. The results show a significant improvement in interfacial energy of the hydroxyapatite films on the Ti6AL4V substrates over the C.P. titanium substrates with the anodised 25 volt and 50 volt Ti6Al4V substrate yielding values of 12.1 and 12.8 J/m^2 compared with values of less than 2 J/m^2 for the C.P. titanium samples.

Experimentation also shows that for both C.P. Titanium and Ti6Al4V substrates the 25 and 50 volt anodised samples for the crack free zirconia have interface toughness values in excess of 1.5 $MPa.m^{1/2}$ in addition to them the Ti6Al4V substrate also is in excess of 1.5 $MPa.m^{1/2}$ indicating that these samples all possess good interface toughness values while the other substrates have toughness values half the previously mentioned samples of about 0.75 $MPa.m^{1/2}$.

The zirconia solution used was modified with 1- Butanol to reduce the viscosity of the zirconia sol gel to 10 -12 centipoise and this lead to the formation of a crack free zirconia coating of 100 nm thickness when spin coated, also the tetragonal polymorph was found on all substrates tested with X–ray diffraction.

Tribological results on the zirconia-coated titanium samples, both anodised and control, showed the titanium samples yielded better wear-resistance properties than the double coated samples. The 50 volt anodised titanium samples yielded the best wear resistance of all samples tested after 500,000 cycles on the Ortho-pod machine in water.

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

V	Volts
A	Constants
B	Constants
σ_c	Critical stress for cracking (MPa)
ε_c	Strain at first cracking
E_f	Young's Modulus of film (MPa)
σ_r	Residual Stress
λ_f	Fracture energy of film (Jm^{-2})
g(α)	Constant
α	Dundas parameter
K_{ic}	Film toughness ($MPa.m^{1/2}$)
d	Oxide thickness
ε	Strain
σ	Stress (MPa)

PUBLICATION LIST

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